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Life cycle assessment and process development of photobiological hydrogen production – From laboratory to large scale applications

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Abstract

Hydrogen as an energy carrier becomes more important in a future sustainable energy economy. One regenerative hydrogen production path is photobiological production by green algae "Chlamydomonas reinhardtii". This organism is proven to produce small amounts of hydrogen under certain conditions only using sunlight and water [1]. To get into competition to other production technologies a new organism, called "Design Cell", should overcome the handicaps of green algae leading to an improved organism.

For cultivation of the microorganisms a photobioreactor system was developed in a laboratory scale. To collect first technical data a system analysis based on the methods of life cycle assessment was conducted to classify the current status of photobiological hydrogen, to identify potentials and to uncover weaknesses. The results were compared with other ways of hydrogen production. To develop the process to large scale applications, hydrogen production rates under sunlight illumination are estimated and a large scale reactor was designed.

The assessment showed that the actual hydrogen production rates have to be increased at least by a factor of 100 to get into competition to other technologies. Scale up and sunlight illumination tests showed a lot of optimization potential, but also system limitations for large scale applications.

Keywords: Life cycle assessment; photobioreactor; green algae; cyanobacteria; photobiological hydrogen

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1. Introduction

Scarcity of fossil fuel resources, a high amount of greenhouse gas emissions and a growing world population are topics leading to a rethinking for a future energy economy. To deal with this challenges the German Government determined a program in 2010 to reduce the greenhouse gas emissions in Germany until 2020 about 40% and until 2050 about 80% referred to the emissions in 1990 [2]. Within this program, beneath the substitution of fossil fuels with renewable energies, the increasing of energy efficiencies and the extension of the electricity grid, the research and development of new and innovative techniques is essential.

In this context hydrogen is seen as a key factor in the future energy economy. But, since hydrogen in nature only exists as compound, it has to be gained from other resources. Today almost everything of the world's 600 billion Nm^3 hydrogen produced per year is gained from fossil fuels, especially over steam methane reforming [3]. To be environmental compatible over the whole life cycle, hydrogen must be produced without fossil fuels. Here electrolysis of water could be one option, but conversion losses at the electrolyser, hydrogen storage and the re-electrification reduce the overall efficiency of this process and the electricity for electrolysis has to come from regenerative energies. Another possibility is the usage of biological processes for hydrogen production as they appear in a multitude of microorganisms. The processes to produce hydrogen biological are manifold. This paper focusses on organisms that use light energy from the sun to produce hydrogen over photosynthesis.

The research on this so called photobiological hydrogen production is at the beginning. In this research project an interdisciplinary cooperation of engineers, biologist and chemists investigate the potential of this technique and try to develop it. Most important is to figure out if the production of photobiological hydrogen in an appropriate industrial scale is competitive to other hydrogen production technologies and what shortcomings have to be resolved. The classification with other technologies and the determination of scaling factors is realized over key figures determined with a Life Cycle Assessment. But also the genetic optimization of the microorganisms, the design of an effective photobioreactor and the test of long term cultivation of the microorganisms are essential.

2. Principals

The interest on photobiological hydrogen production is founded on the fact that the resources for this process, sunlight and water, are available almost everywhere in the world. It reaches back to the year 1939 where the German biologist Hans Gaffron discovered that green algae are able to produce hydrogen over its photosynthetic apparatus under certain conditions. By now cyanobacteria and green algae are the only known organisms with the ability of oxygenic photosynthesis and hydrogen production. [4] One of these organisms is the unicellular green algae "Chlamydomonas Reinhardtii".

The process of photobiological hydrogen production is related to photosynthesis (figure 1). Usually under influence of sunlight in the algal cell water is split at the Photosystem II (PSII) into oxygen, protons and electrons. Simplified, these light-driven electrons move from PSII to Photosystem I (PSI) and from there to the CO_2-fixation and biomass generation in the cell. Under sulphur deprivation, the metabolism of the green algae switches from natural oxygen production and CO_2-fixation to hydrogen production [1]. In that case an enzyme, called hydrogenase (H_2ase), is activated what is able to catalyze a hydrogen evolution with high specific activity. Evolutionary this process is activated to have an electron sink in the cell at the H_2ase if the CO_2-fixation is inactive to keep the organism alive under deprivation conditions. [5] The H_2ase uses the electrons that would usually move to the CO_2-fixation to generate hydrogen. The

process of photosynthetic electron transport in green algae can operate with a photon conversion efficiency of approximately 85-90% [6].

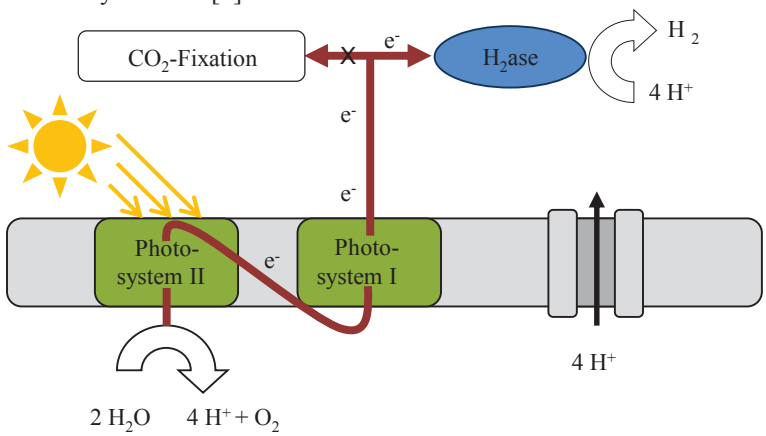

Fig. 1: Simplified hydrogen production process within photosynthetic apparatus of green algae

The main problem using unicellular green algae, like “Chlamydomonas reinhardtii”, is the sensitivity of their high productive H_2ases to oxygen, which is an auxiliary product of the process. For that reason, the natural hydrogen production only takes place under anaerobic conditions and only for short periods of time. But in respect to a commercial use of photobiological hydrogen this cannot be a promising way. In respect to those restrictions the green algae is actually able to produce 5 ml hydrogen per liter algae suspension and hour [7].

To overcome this disadvantage, biologists in this research project are going to establish a new form of “Design Cell” on a biotechnological way based on the cyanobacteria “Synechocystis spec. PCC 6803”. This organism has naturally a very effective system for assimilation of DNA and methods for its genetic manipulation are well known. [8]

By establishing this “Design Cell” some points are of special importance. First the H_2ases of the cyanobacteria are of low activity and have to be replaced by an oxygen resistant and high productive H_2ase. Then the electron transport in the cell has to be optimized, so that the majority of the electrons from water splitting are used for hydrogen production and not for CO_2-fixation and biomass production. Also the “Design Cell” has to be flexible for changing conditions and applicable for cultivation in future mass production systems. At least the hydrogen production rate has to be increased to a level where the photobiological hydrogen production can compete with other hydrogen production technologies.

3. Photobioreactor system

For microorganism cultivation and hydrogen production photobioreactor systems are used. For different applications a variety of photobioreactor systems are available, ranging from open pond systems, closed tubular systems to flexible tube systems. Within this project a closed flat plate reactor was chosen, because it provides optimal conditions for hydrogen production, cultivation and upscaling. The reasons for choosing this type of reactor system was, that only in closed reactors the capture and subsequent storage of hydrogen can be realized and that the organisms are protected from uncontrolled contamination. Also the regulation system parameters are easier to handle and it promises best conditions for illumination, nutrient supply and suspension mixing.

Until now, photobioreactors are developed for laboratory use only. The installation is vertical to allow an illumination from both sides with a small depth (4 cm) what enlarges the light entry and minimizes the

utility space to less than one meter. The reactor works in a continuous mode and mixing of the algal suspension is realized over two gas inlets at the bottom of the reactor where a mixture of nitrogen and carbon dioxide is pumped into the reactor. Mixing of the algal suspension is important, because a static suspension forces shadowing effects between the organisms and, as a consequence of this, the hydrogen production rate will be negatively influenced. Also a continuous carbon dioxide supply is necessary to keep the metabolism of the organisms alive.

In a first step a twelve-liter PBR consisting of a steel frame and two glass panels was developed. This reactor was operated in batch mode. For the "Design Cell" a new reactor was designed made out of materials that are cheaper and the new system should work in a continuous mode in respect of a future mass production. The new reactor system is made out of plastics and has a volume of 5 liters. The reactor includes instruments for heating, sensors for pH, turbidity and temperature control, a light bank for illumination and a system control unit (figure 2). Long time studies showed that a continuous cultivation can operate for more than 300 days a year, before it must be stopped for cleaning and maintenance.

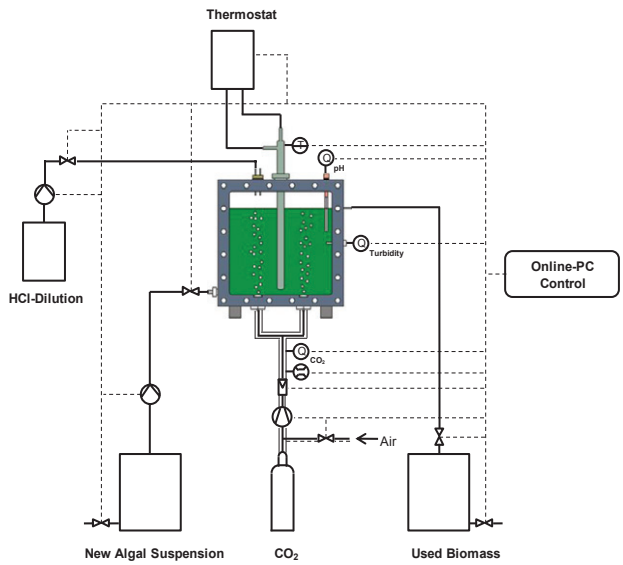

Fig. 2: Scheme of photobioreactor system

For future large scale applications the existing photobioreactor system was upscaled to increase the total reactor volume and according to this the hydrogen production rate. Main aspects that were focused on within upscaling were that the reactor system has a size that is constructional easy to handle and that maintenance and connection with additional reactors could be realized without much complexity. The prototype of that large scale bioreactor was upscaled from a suspension volume of 5 liter to a volume of 100 liter with the same reactor depth as the small reactor (figure 3). This new reactor system also uses the same auxiliary and measuring systems as the small reactor and can also be completely controlled online. Actually the upscaled system is used for operating and cultivation tests.

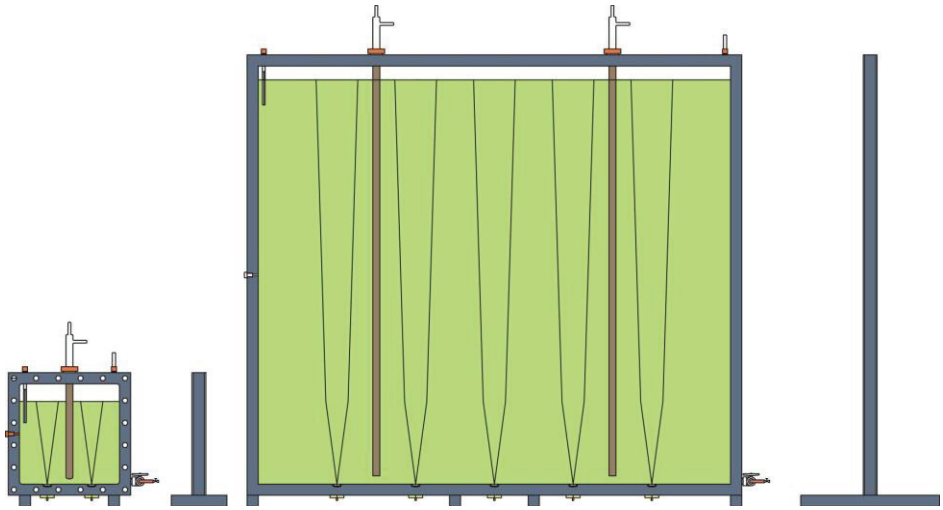

Fig. 3: Comparison small and upscaled reactor [9]

4. Process Assessment

As mentioned before to be environmental compatible the production process of hydrogen must be independent from fossil fuels. To assess a process over the whole life cycle an appropriate method is a Life Cycle Assessment or ecobalance. In case of the photobiological hydrogen production as a technology in an early development status it is interesting to see where weaknesses are and where the focus has to lie in ongoing research. For this reason both bioreactor systems are evaluated and compared with other hydrogen production technologies. Also the photobioreactor system are compared together to figure out possible scale up effects.

4.1. Life Cycle Assessment

The different steps of a Life Cycle Assessment (LCA) are defined in the international standards DIN EN ISO 14040 [10] and DIN EN ISO 14044 [11]. The assessment of the PBRs is orientated towards these standards.

For the assessment of different hydrogen production technologies the functional unit, to which the results are related to, was defined as one MJ of produced hydrogen. During the Life Cycle Inventory Analysis all material, energy and emission flows (inputs and outputs) of the production and using phase are measured and lead to the Life Cycle Inventory Analysis result. Gaps of data were filled with assumptions on basis of corresponding literature. Specific energy expenditures and produced emissions were linked to the Inventory Analysis result. As database to calculate the Life Cycle Impact Analysis the Ecoinvent database [12] and the database of the balancing software GaBi [13] were used. The linking of Life Cycle Inventory Analysis and the data from Ecoinvent and GaBi was modeled with the balancing software GaBi 4 [14], where the Ecoinvent database and the GaBi database are implemented.

Within the Impact Assessment, impact categories as well as specific indicators are defined. The inputs and outputs are classified by these impact categories. Using characterization factors based on the method of CML 2001 [15], the impact category indicators are calculated. The leading indicator that was calculated is the Cumulated Energy Demand (CED). This indicator sums up every energetic input over

the life cycle of the process related to primary energy. The second indicator is the Global Warming Potential (GWP), what describes the anthropogenic global warming effect. Further indicators, such as the Eutrophication Potential (EP) and the Acidification Potential (AP) were calculated. In this context, the EP (measured in kg PO_4^{3-}-Equivalent) indicates emissions leading to an overfertilization of ground and waterbodies. Furthermore, the AP (measured in kg SO_2-Equivalent) announces acidic emissions into the air leading to acid rain. Indicators GWP, AP and EP are used to characterize the environmental impacts a product system generates over its lifetime.

Data for the assessment of photobiological hydrogen production was collected from the manufacturer of the PBR and measured during the operation of the photobioreactor. The period under observation is ten years. Beneath the actual data from the laboratory 5 l – PBR and the upscaled reactor, another photobiological path has been calculated. For this scenario it is assumed that the hydrogen production rate will be increased by the factor of 100, cultivation will be realized in scaled up reactors with reduced energy demand and under sunlight illumination. Other hydrogen production technologies for a benchmark are steam methane reforming, biomass gasification, wind electrolysis, bio-/sewagegas reforming, photovoltaic electrolysis and electrolysis over net electricity. The results for the assessment of the benchmark technologies are taken from Petrovic [16, 17].

4.2. Results

The results of the LCA for the actual photobioreactor systems were separated in three life cycle parts. The production, the operation and the disposal phase of each photobioreactor. The results of any impact factor showed for both photobioreactor systems, that their whole life cycles are dominated by the operation phase. Figure 4 illustrates the results for the upscaled system. For the small scale reactor the relative results show the same trends. The absolute results for the upscaled system are of course higher related to the small scale system.

Most dominant part in the operational phase is the process energy demand with approximately 80% of every impact factor. Here sterilization of process water, artificial illumination, temperature control and carbon dioxide supply have the largest impacts. The results show that the cultivation of microorganisms and the operation of the process itself need a lot of energy supply. For the actual systems the supplied energy for operation processes is related to net electricity mix of Germany. In consequence of this the environmental impact factors are also dominant in the operation phase, because German electricity mix depends about two third on fossil fuels.

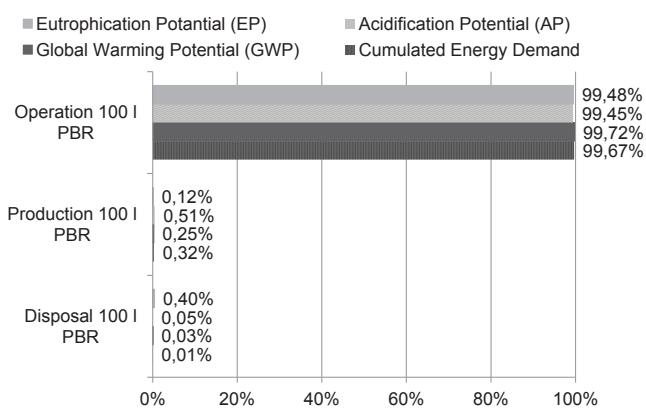

Fig. 4: Relative impact factors over life cycle for upscaled 100 l - reactor

For future photobiological bioreactor systems it is necessary to optimize the process by reducing the energy demand of different process parts. Options here are first of all using sunlight for illumination instead of artificial light. For this the behavior of microorganisms under changing light conditions and light intensities have to be investigated. Also a sterilization method for process water that is less energy intensive, for example chemical sterilization, has to be taken under consideration. In future commercial production plants it is self-evident that more energy efficient process parts will be used that would also reduce the overall energy demand.

The specific impact indicators of the small and upscaled photobioreactor systems are shown in Figure 5, with the results of the future scenario (Optimized photobioreactor system) and competing hydrogen production technologies for a benchmark. Obviously it can be seen that photobiological hydrogen production today is not competitive in every impact category to competing production processes. But a considerable optimization potential can be seen in upscaling the reactor size, because impact indicators reduce in every category between the small and upscaled reactor. So an increasement of energy efficiency from laboratory to large scale applications can be expected.

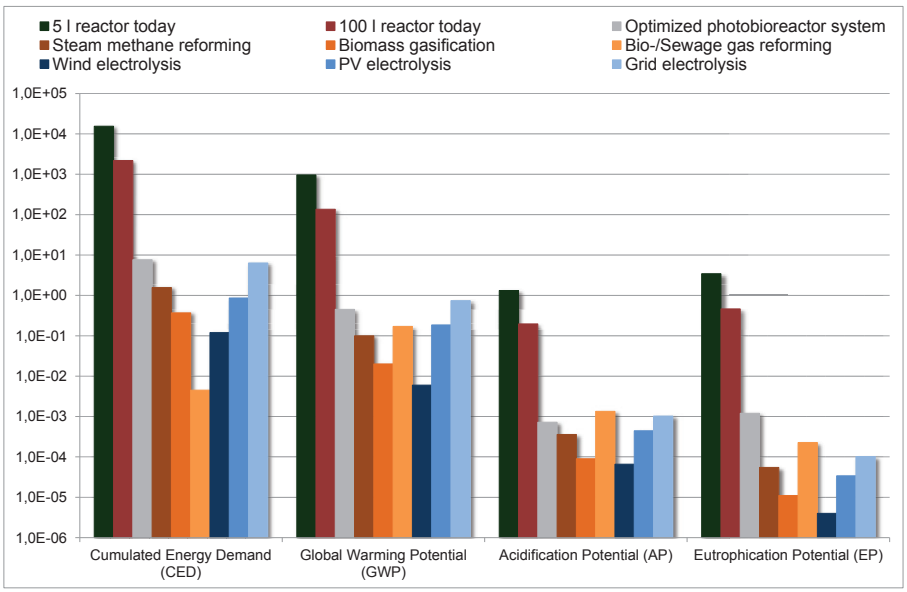

Fig. 5: Benchmark of specific impact indicators per MJ-H_2

Looking at the optimized photobiological scenario, which includes a hundredfold increased hydrogen production rate and reduced energy demand for process operation, the photobiological hydrogen production becomes competitive to other technologies (grey column). The ecological indicators excluding the EP of the scenario are yet competitive, almost to Steam Methane Reforming and Electrolysis via Grid Electricity. The actual disadvantage of photobiological hydrogen must be related to the laboratory status of this technology, the momentarily low hydrogen production rates and the low energy efficient photobioreactor system.

5. Conclusions

A regenerative path to produce hydrogen is the photobiological hydrogen production by the green algae “Chlamydomonas reinhardtii”. It is proven that this organism is able to produce hydrogen under

certain conditions. The development of photobiological hydrogen production today is on a basic research level. To get into competition to other hydrogen production technologies drawbacks of the green algae, like oxygen sensitivity of their hydrogen production enzyme hydrogenase have to be negotiated. For that reason, a new form of "Design Cell" based on cyanobacteria should overcome the handicaps of the green algae leading to an improved and compatible organism.

For cultivation of hydrogen-producing organisms a small, laboratory photobioreactor and an upscaled photobioreactor are developed that are cheap, modular and optimized for illumination and mixing. The photobioreactors consist of synthetic materials and have volumes of five liters and 100 liters. The reactors include instruments for heating, sensors for pH control, turbidity and temperature, a light bank for illumination and a system control unit.

A Life Cycle Assessment of both photobioreactor systems was established to determine technical and economical key figures. The intention of this assessment on a very early development stage was to collect first technical data in order to classify the current technological status of the photobiological hydrogen production, to identify potentials and to uncover weaknesses. Also the scale up effects between laboratory and large scale reactors were under investigation. The results were compared with other ways of hydrogen production, like steam methane reforming or wind electrolysis.

This assessment has shown that the photobiological hydrogen production with green algae, the current hydrogen production rate and the laboratory reactors are not competitive compared to other hydrogen production techniques at this stage of development. However, upscaling from small to large scale applications showed significant scale up effects. The assessment also pointed out, that the whole process is dominated by the operation phase and here especially by water sterilization and artificial illumination. For future applications, alternatives for energy intensive process parts have to be found.

Further calculations with a scenario of an increased hydrogen production rate in a scaled up photobioreactor show that the photobiological hydrogen production can compete with other regenerative hydrogen production paths with a production rate that is at least a hundred times higher than today. Biologists that are working in this research project are optimistic to reach a production rate with the new "Design Cell" that satisfies these requests. But to get to a large-scale photobiological hydrogen production still more research activities are necessary.

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